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The Absence of CDW order in PbSb, and its unexpected softness

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Abstract

We have performed an ab-initio calculation of the electronic structure of PbSb. Since Sb usually takes 3- valence state in a compound, Pb in PbSb formally takes 3+ valence state, which is very unusual. The stable valences of Pb are 2+ and 4+, and Pb^{3+} state is unstable and may have large charge fluctuation. This type of "valence-skip" fluctuation can induce charge-density-wave or superconductivity. However, our calculation shows that the valence of Pb is 2+ or smaller. We have also found that PbSb is one of the "softest metals" except for the alkali metal elements.

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1. Introduction

Pb atoms in a compound usually take 2+ or 4+ valence state, and hardly take 3+ valence state. If we put the Pb atom into a site where it should take 3+, this valence state is unstable and may have large charge fluctuations. This type of "valence-skip" charge fluctuation can induce a charge-density wave (CDW) or superconductivity[1]. The most famous example is $BaBiO_3$. In this compound the average valence of Bi is 4+, but with the instability of Bi^{4+} state, charge disproportionation such as $2Bi^{4+} \rightarrow Bi^{3+} + Bi^{5+}$ occurs. This charge disproportionation (or CDW) accompanies a lattice distortion[2], and this lattice distortion (mainly breathing type) may be necessary to induce CDW[1,3-5]. Carrier doping such as $Ba(Pb_xBi_{1-x})O_3$ or $(Ba_{1-x}K_x)BiO_3$ can melt this CDW and induce superconductivity[2,6,7]. In this superconducting phase, the lattice distortion is eliminated and Bi has only one crystallographic site. In other words, in the superconducting phase Bi is forced to take Bi^{4+} (despite of the small imbalance due to the carrier doping), which should induce a large charge-fluctuation.

It is interesting to search a new superconductor like $(Ba_{1-x}K_x)BiO_3$. InTe might be also in this category, because indium has the unstable valence In^{2+} on average. In ambient pressure indium occupies two different crystallographic

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sites, and forms the CDW state. Under high pressure InTe has the cubic NaCl structure. In this high-pressure phase, InTe shows superconductivity below 3.5K[8]. We have noticed that PbSb[9] has the NaCl structure even in the ambient pressure. Therefore PbSb may be one of the candidates of the valence skipper, because Sb usually takes 3- valence, and Pb is forced to take 3+ valence state due to the charge neutrality.

However, it is not trivial whether Pb takes 3+ valence state on average or not, because the difference of the electronegativity between Pb and Sb is not so large. In this paper, we have calculated the electronic structure of PbSb from first-principles. Since the binding energy of the Pb-s state is very large and the states near the Fermi level mainly consist of the Sb-p states, eventually the valence of Pb is fairly smaller than 3+. Moreover, we have found that PbSb has a very small bulk modulus, which shows that PbSb is one of the "softest metals" except for alkali metal elements.

2. Method of calculations

We have calculated the electronic structure of PbSb from first-principles. We have used a full-potential augmented plane-wave (FLAPW) scheme and the exchange-correlation potential was constructed within the local-density approximation (LDA). These are implemented as KANSAI-94 and TSPACE[10] computer codes. Spin-orbit interaction is included via second-variational scheme[11]. The space group is fixed to Fm-3m (#225), and the lattice constant has been scanned through the experimentally observed one[9] and repeated the calculation of the electronic structure. Muffin-tin radii are set as r(Pb)=r(Sb)=0.204*a*, where *a* denotes the lattice constant. For the plane wave basis functions we used about 200 LAPWs.

3. Results and Discussions

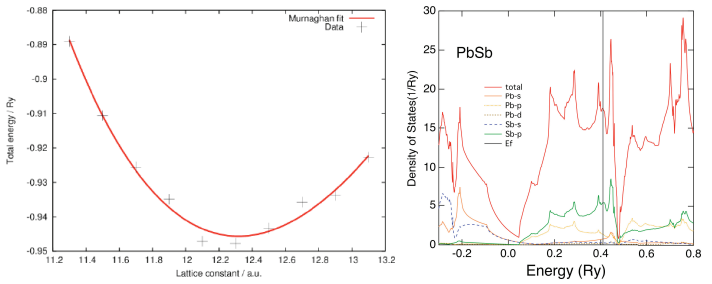

Fig. 1. (a) *a*-dependence of the total energy; (b) DOS curve of PbSb.

First we discuss the elastic properties of PbSb. Figure 1(a) shows the lattice parameter (*a*) dependence of the total energy in this calculation. We have obtained the equilibrium lattice constant as *a*=6.535Å. This value is ~5% larger than the experimental value. It is known that the equilibrium lattice constant obtained by LDA calculation is usually smaller than the experimental one. This discrepancy is probably due to the metastable nature of PbSb. We fit the *a*-dependence of the total energy using the Birch-Murnaghan equation of states, and obtained the bulk modulus B=11.7GPa. This value is much smaller than the element Pb (B=45.6GPa) and the element Sb (B=42GPa). PbSb may be one of the "softest metal", the bulk modulus of PbSb is comparable with element Ba (B=9GPa), which is the softest element metal except the alkali metal[12,13].

Figure 1(b) shows the density of states (DOS) curve of PbSb. We can see that the states with energy range -0.3~-0.2Ry mainly consists of the Sb-s state. Similarly, the states with energy range -0.2~0.05Ry and 0.05~0.45Ry (valence band) mainly consist of the Pb-s and Sb-p states, respectively. The states with an energy range of 0.45~0.8Ry (conduction bands) mainly consist of the Pb-p states. These bands are mutually well hybridized, reflecting the extended nature of the 5s,p and 6s,p orbitals. The DOS at the Fermi level is $D(E_F)$=17.5Ry/u.c., which corresponds to the electronic specific heat coefficient γ(cal)=3.03mJ/molK^2. The DOS curve has a dip at the Fermi level (E_F), thus a small off-stoichiometry can enhance DOS if we can use the rigid-band model. Especially for electron doping, 0.033Ry upward shift of E_F (0.55 electrons doping) raises $D(E_F)$ up to a peak, and $D(E_F)$ reaches 25.6Ry (50% larger than PbSb).

Figure 2 shows the energy dispersion (E(k)) curve of PbSb. The left panel and the center panel correspond to the calculation with and without spin-orbit interaction (SOI), respectively. The magnitude of the SOI near E_F is quite large

(~0.1Ry), reflecting the large SOI in the Sb-5p orbitals. We also tried to fit this E(k) curve without SOI by a tight-binding model. The parameters shown in Table I can describe the overall structure of the valence bands and the conduction bands (as shown in the right panel of Fig.2. The number markers seen in the center and the right panel denote the irreducible representation. Our fitting is successful not only for E(k) but also for the irreducible representations).

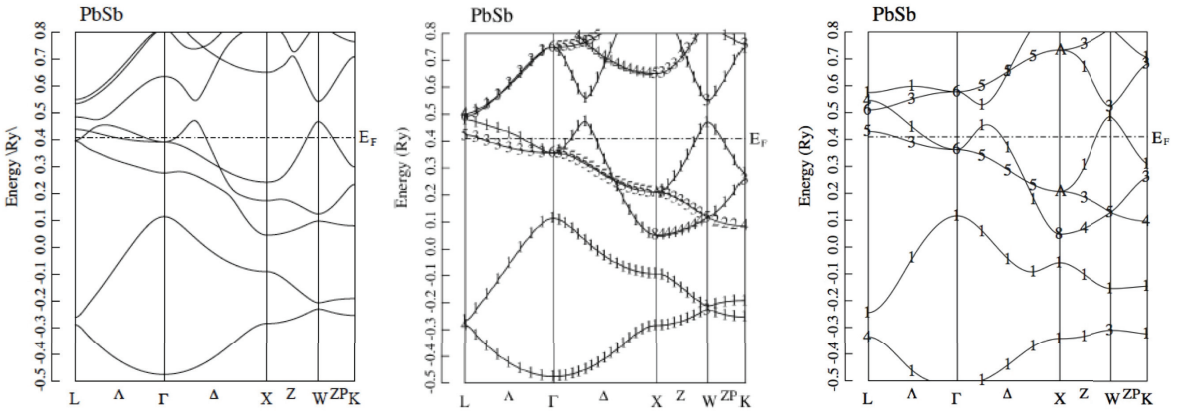

Fig. 2. Energy dispersion curves of PbSb.

We can see that the Sb-p orbital is slightly deeper in energy than the Pb-p orbital. Moreover, the Pb-s orbital is well deeper than the Sb-p orbital, therefore the charge balance in PbSb becomes like $Pb^{+(2-d)}Sb^{-(2-d)}$, where *d* denotes the number of electrons of the back donation from the Sb-p orbital due to the strong hybridization between the Sb-p and Pb-p orbitals. The reason why Pb-6s orbital has such a large binding energy is the relativistic effect, which is effective in heavy atoms.

Next we discuss the possibility of the valence skip in this compound. As mentioned in the introduction, if an atom is forced to take unstable valence, a large charge fluctuation is expected. Formally Pb^{3+} has the electron configuration $[Xe](4f)^{14}(5d)^{10}(6s)^{1}$, having an open shell $(6s)^{1}$. However, our calculation shows that the Pb-6s orbital is almost completely occupied due to its large binding energy, thus valence-skip cannot be expected in PbSb. Let us compare the "isovalent" compounds InTe and PbSb (They have the same number of valence electrons)[14]. In InTe, In5s orbital has smaller binding energy because In is lighter than Pb. Moreover, Te5p has larger binding energy than Sb5p. Our calculation for NaCl-type InTe shows that In-5s orbital has much smaller binding energy, and at the In-5s partial DOS at E_F is very large, comparable to the Te-5p partial DOS. Therefore we can assume a simple ionic configuration of $In^{2+}Te^{2-}$ for NaCl-type InTe. This is probably one of the reasons why the CDW state occurs in InTe but not in PbTe.

Table 1. tight-binding parameters of PbSb. The units are all Ry.

Orbital	orbital energy	Transfer (Pb,Sb,symmetry)	transfer energy
Sb-s	-0.30	(ssσ)	0.05
Pb-s	-0.10	(spσ)	0.09
Sb-p	0.43	(psσ)	0.05
Pb-p	0.51	(ppσ)	0.13
		(ppπ)	-0.04

4. Summary

The electronic structure of PbSb has been calculated. PbSb formally satisfies the condition of valence skipping, namely has Pb^{3+}, but our calculation shows that Pb-6s orbital has too large binding energy to realize the Pb^{3+} valence state. In the formation of valence skipping, important thing is not only formal charges but also the binding energy of the cation s- orbital. PbSb is probably one of the "softest metals", except for alkali metals.

Acknowledgements

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